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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

RECD 16 FEB 2005

Applicant's or agent's file reference CL2079PCT	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US 03/24117	International filing date (day/month/year) 31.07.2003	Priority date (day/month/year) 09.08.2002
International Patent Classification (IPC) or both national classification and IPC C23C16/00		
Applicant E.I. DU PONT DE NEMOURS AND COMPANY et al		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 8 sheets, including this cover sheet.

This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 6 sheets.

3. This report contains indications relating to the following items:

- I Basis of the opinion
- II Priority
- III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV Lack of unity of invention
- V Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI Certain documents cited
- VII Certain defects in the international application
- VIII Certain observations on the international application

Date of submission of the demand 01.03.2004	Date of completion of this report 17.02.2005
Name and mailing address of the International preliminary examining authority: European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer Seitner, I Telephone No. +31 70 340-2389



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I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1-15 as originally filed

Claims, Numbers

1-29 filed with telefax on 04.01.2005

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- the language of publication of the international application (under Rule 48.3(b)).
- the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- contained in the international application in written form.
- filed together with the international application in computer readable form.
- furnished subsequently to this Authority in written form.
- furnished subsequently to this Authority in computer readable form.
- The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- the description, pages:
- the claims, Nos.:
- the drawings, sheets:

5. This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

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IV. Lack of unity of invention

1. In response to the invitation to restrict or pay additional fees, the applicant has:

- restricted the claims.
- paid additional fees.
- paid additional fees under protest.
- neither restricted nor paid additional fees.

2. This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is

- complied with.
- not complied with for the following reasons:

see separate sheet

4. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report:

- all parts.
- the parts relating to claims Nos. .

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	1-6,14-29
	No: Claims	7-13
Inventive step (IS)	Yes: Claims	18-29
	No: Claims	1-17
Industrial applicability (IA)	Yes: Claims	1-29
	No: Claims	

2. Citations and explanations

see separate sheet

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Reference is made to the following documents:

D1: HISASHI TANAKA AND OSAMU YAMAUCHI: "Über die Synthese und Chelatkomplexe von 2-Pyrrolylmethyleniminen. II." CHEMICAL & PHARMACEUTICAL BULLETIN, vol. 10, no. 6, 1962, pages 435-439, XP008025701

D2: B EMMERT ET AL: "Über innere Komplexsalze einiger Pyrrol-Derivate" CHEMISCHE BERICHTE, vol. 62, 1929, pages 1733-1738, XP008025676

D3: YEH K-N ET AL: "SYNTHESIS AND PROPERTIES OF SOME METAL CHELATES OF 2-PYRROLEALDIMINES" INORGANIC CHEMISTRY, AMERICAN CHEMICAL SOCIETY, EASTON, US, vol. 6, no. 4, 1967, pages 830-833, XP000915350 ISSN: 0020-1669

D4: HISASHI TANAKA AND OSAMU YAMAUCHI: "Über die Synthese und die Chelatkomplexe von N-2-Pyrrolylmethylenaminen. I." CHEMICAL & PHARMACEUTICAL BULLETIN, vol. 9, 1961, pages 588-592, XP008025628

D5: DATABASE CAPLUS [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; KROWCZYNSKI, ADAM ET AL: "Metal complexes of pyrrole derivatives and method of their preparation" XP002265131 retrieved from STN Database accession no. 129:349117

D6: EP-A-1 170 308 (MITSUI CHEMICALS INC) 9 January 2002 (2002-01-09)

D7: DATABASE CAPLUS [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; HONDA, KENJI ET AL: "Polymeric pyrrole derivatives. 9. Reactions between copper complexes containing pyrrole Schiff bases and 2,2-diphenyl-1-picrylhydrazyl" XP002265132 retrieved from STN Database accession no. 81:106212

D8: DATABASE CAPLUS [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; TOMONO, TSUGIKAZU ET AL: "Synthesis and polymerization of copper(II) and cobalt(III) complexes containing 3-(2-

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pyrrolylmethylenimino)prop-1-ene or p-(2-pyrrolylmethylenimino)styrene"
XP002265133 retrieved from STN Database accession no. 81:50107

D9: GORDON L EGGLETON ET AL: "Oxygen-17 and Carbon-13 Nuclear Magnetic Resonance Spectra of Thiophene- and Pyrrole-2-carboxaldehyde. Condensation Products Prepared From Ephedrine Derivatives" JOURNAL OF HETERO CYCLIC CHEMISTRY, vol. 27, no. 1853, 1990, pages 1853-1855, XP002265130

D10: US-A-5 464 666 (FINE STEPHEN M ET AL) 7 November 1995 (1995-11-07)

D11: US-A-3 594 216 (CLEARY JAMES G ET AL) 20 July 1971 (1971-07-20)

Re Item IV

Lack of unity of invention

According to Rule 13.1 PCT, "The International application shall relate to one invention only OR to a group of inventions so linked as to form a single general inventive concept".

This is further clarified in Rule 13.2 PCT, which details that "the requirement for unity of invention shall only be fulfilled when there is a technical relationship among those inventions involving one or more of the same corresponding special technical features that defines a contribution which each of the claimed inventions, considered as a whole makes over the prior art".

It is considered that the problem to be solved by the present application is the provision of a further process for depositing copper.

The solution is provided by the use of compounds according to structure 1 of claim 20. Thus, the single general concept can be identified as the provision of a further process for depositing copper by using compounds according to structure 1 of claim 20.

Present claims 1-17 relate to general processes for the preparation of pyrrolealdimines ligands or the respective Cu(II)-complexes.

Claim 18 and 19 cover a limited number of compounds falling within the scope of the

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general structure 1 of claim 20.

Claims 20-25 and 28 refer to the actual process for depositing copper on a substrate and claims 26, 27, and 29 to the corresponding substrate with the Cu(II) complex.

However, the general processes of claims 1-17 concern the preparation of known compounds (see for example, in D3: compounds IIb-IIe, IIIb-IIIe; in D9: Fig 1, compound 2;).

Therefore, insofar as the processes of claims 1-17 do not cover the preparation of compounds as claimed in claims 18 and 19, it is considered that said claims address problems distinct to the general common concept, namely the provision of processes for the preparation of pyrrolaldimines or Cu(II)-complexes with 2-pyrrole derivatives.

Consequently, there is not one general concept which could link the different inventions of the present application and the requirement of unity of invention is not complied with.

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

V.1. Novelty:

The process for chemical vapour deposition according to present claim 20 has not been disclosed in the prior art. Therefore, the subject matter of **claims 20-29** is considered **novel (Article 33(2) PCT)**.

The compounds of claim 18 and 19 have not disclosed in the prior art and therefore the subject matter of **claims 18 and 19 is novel (Article 33(2) PCT)**.

The prior art does not disclose the processes according to claims 1 and 14 and the subject-matter of **claims 1-6 and 14-17 is therefore novel (Article 33(2) PCT)**.

Documents D3 and D7 disclose processes for the preparation of Cu(II) complexes of pyrrolaldimines anticipating the novelty of the presently claimed process of claims 7. Therefore, the subject-matter of **claims 7-13 is not considered novel under Article 33(3)**

PCT.

V.2. Inventive step:

Documents D10 and D11 which are considered as the closest prior art for the subject matter of claim 20 disclose chemical vapour deposition using copper complexes from which the complexes of the present application differs in that pyrrolyl ligands are employed.

The problem to be solved can be considered as the provision of a further process for depositing copper. The solution provided by the compounds of structure 1 according to claim 20 comprising pyrrolyl ligands can not be derived in an obvious way from the teaching of the prior art.

The subject-matter of **claims 20-29** and the subject-matter of **claims 18-19**, relating to the novel copper complexes to be used in the deposition process are therefore considered as involving an **inventive step** in the sense of **Article 33(3) PCT**.

Document D1 which is considered as the closest prior art for claims 1-6, discloses a process for the preparation of pyrrolaldimine derivatives via a condensation reaction which differs from the one described in claim 1, in that no extra water-immiscible organic compound is added to the reaction mixture (see page 438). However, the skilled person would regard it as a normal work-up method to add an organic solvent to form a 2 phase-mixture. Moreover, the addition of benzene to this kind of reaction mixture is suggested in D9 (see page 1854, second paragraph).

Therefore, the subject-matter of **claims 1-6** is not considered as involving an **inventive step (Article 33(2) PCT)**.

Document D2 describes (see page 1737) the formation of pyrrolaldehyd copper complexes using copper oxide. Even though D2 concerns 2-formylpyrroles and not 2-acylpyrroles as in claim 14, it would have been obvious to the skilled person to apply the teaching of D2 concerning the aldehydes to the closely related ketone compounds. The process of claim 14 is therefore regarded as suggested by the prior art. The subject-matter of **claims 14-17** does therefore not involve an **inventive step** in the sense of **Article 33(3) PCT**.

It is however noted that those parts of the process-claims 1-17 which relate to the

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preparation of novel compounds, can be considered as novel and inventive under Articles 33(2) and 33(3) PCT, insofar as those novel compounds are used in the novel and inventive process for depositing copper according to claim 20.

V.3. Industrial Applicability:

The present application relates to a process for chemical vapour deposition, the complexes used therein and processes for preparing pyrrolaldimines and their Cu(II) complexes. The subject matter of **claims 1-29** is therefore considered as **industrially applicable (Article 33(4) PCT)**.

CLAIMS

What is claimed is:

1. A process for preparing pyrrolealdimines, comprising the steps of:
 - 5 a) reacting 2-formylpyrrole with a primary amine, RNH_2 , in an aqueous solution, wherein R is C_1 to C_{10} alkyl or substituted alkyl, or C_6 to C_{12} aryl or substituted aryl;
 - b) adding a water-immiscible organic compound to form an aqueous phase and an organic phase; and
 - 10 c) isolating the organic phase.
2. The process of Claim 1 wherein R is methyl or phenyl.
3. The process of Claim 1 wherein the water-immiscible organic compound is selected from the group consisting of alkanes, chlorinated alkanes, cycloalkanes, and aromatic solvents.
- 15 4. The process of Claim 3 wherein the water-immiscible compound is selected from the group consisting of pentane, hexanes, heptanes, chloroform, dichloromethane, carbon tetrachloride, cyclopentane, cyclohexane, benzene, and toluene.
5. The process of Claim 1, wherein the molar ratio of 2-formylpyrrole to primary amine is between about 1:2 and about 2:1.
- 20 6. The process of Claim 1, wherein the temperature is between about 0 °C and about 100°C.
7. An aqueous process for preparing Cu(II) complexes of 2-pyrrole ligands comprising reacting an aqueous mixture of 2-formylpyrrole, a primary amine, R^1NH_2 , and a source of Cu(II), wherein
25 R^1 is selected from the group consisting of C_1 - C_{10} alkyl or substituted alkyl; C_6 to C_{12} aryl or substituted aryl; allyl; benzyl; NHR^3 ; and NR^4R^5 ; and
30 R^3 , R^4 , and R^5 are independently selected from the group of C_1 - C_6 alkyl or substituted alkyl, and C_6 to C_{12} aryl or substituted aryl.
8. The process of Claim 7, wherein the primary amine is selected from the group consisting of methylamine, ethylamine, propylamine, isopropylamine, n-butylamine, t-butylamine, isobutylamine, 2-ethylhexylamine, aniline, 3-trifluoromethylaniline, β -alanine isopropyl ester, β -alanine ethyl ester and benzylamine.
- 35 9. The process of Claim 7, wherein the molar ratio of 2-formylpyrrole to primary amine is from about 1:1 to about 1:10 and the molar ratio of copper to 2-formylpyrrole is from about 10:1 to about 1:10.

10. The process of Claim 7, wherein the temperature is from about 0 °C to about 100 °C.

11. An aqueous process for preparing Cu(II) complexes of 2-pyrrole ligands comprising

5 a. reacting 2-formylpyrrole and a primary amine in water; and
b. adding a source of copper(II) and allowing the mixture to react to form the copper(II) complex.

10 12. The process of Claim 7, wherein the source of copper(II) is selected from the group consisting of copper hydroxide, copper(II) chloride, copper nitrate, copper sulfate, copper(II) salts of carboxylic acids, and copper alkoxides.

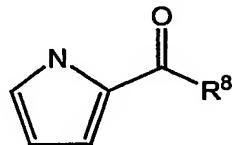
13. The process of Claim 11, wherein the source of copper(II) is copper acetate.

14. The process of Claim 12, wherein the source of copper(II) is copper acetate.

15 15. The process of Claim 7, wherein the reaction is conducted in the presence of a water-immiscible organic compound.

16. An aqueous process for preparing Cu(II) complexes of a 2-acylpyrrole comprising the steps of

20 a. contacting an aqueous mixture of a source of Cu(II) with a 2-acylpyrrole,



25 where R8 is C1 to C10 alkyl; and

b. further reacting the aqueous mixture with a base.

17. The process of Claim 16, wherein the 2-acylpyrrole is 2-acetylpyrrole.

30 18. The process of Claim 17, wherein the molar ratio of 2-acylpyrrole to primary amine is from about 1:1 to about 1:10 and the molar ratio of copper to 2-acylpyrrole is from about 10:1 to about 1:10.

19. The process of Claim 16, wherein the temperature is from about 0 °C to about 100 °C.

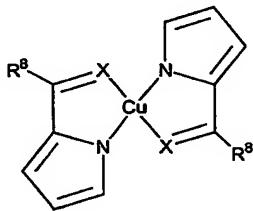
20. A Cu(II) complex comprising:

a) a copper atom; and

5 b) two pyrrole ligands bound to said copper atom, wherein said pyrrole ligands are independently selected from the group consisting of 2-pyrroleald-n-propylimino, 2-pyrroleald-i-butyl-imino, 2-pyrroleald-n-butyl-imino, 2-pyrroleald-2-ethylhexyl-imino, 2-pyrroleald-m-trifluoromethylphenyl-imino, 2-pyrrolylald(2-isopropoxycarbonylethyl)imino, 2-pyrrolylald(2-ethoxycarbonylethyl)imino and 2-pyrroleald-benzyl-imino ligands.

10 21. A Cu(II) complex selected from the group consisting of bis(2-pyrrolylald-n-propylimino)copper(II), bis(2-pyrrolylald-n-butylimino)copper(II), bis(2-pyrrolylaldisobutylimino)copper(II), bis(2-pyrrolylald(2-ethylhexyl)imino)copper(II), bis(2-pyrrolylald(m-trifluoromethylphenyl)imino)copper(II), bis(2-pyrrolylaldbenzylimino)copper(II), bis(2-pyrrolylald(2-ethoxycarbonylethyl)imino)copper(II), bis(2-pyrrolylald(2-isopropoxycarbonylethyl)imino)copper(II), and bis(2-acetylpyrrolyl)copper(II).

15 22. A process for depositing copper on a substrate comprising:
20 a) adsorbing onto a substrate at least one Cu(II) complex of structure 1,
 structure 1 =



25 wherein:
 X is O, and R8 is C1-C10 alkyl or substituted alkyl, or C6 to C12 aryl or substituted aryl; or
 X is NR1 and R8 is H;
 R1 is selected from the group consisting of C1-C10 alkyl or
30 substituted alkyl; C6 to C12 aryl or substituted aryl; allyl; benzyl; NHR3; and NR4R5; and
 R3, R4, and R5 are independently selected from the group of C1-C6 alkyl or substituted alkyl, and C6 to C12 aryl or substituted aryl; and

b) exposing said absorbed complex to a reducing agent to form copper metal.

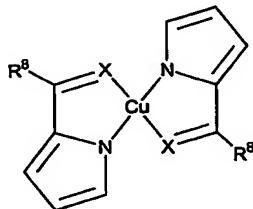
23. The process of Claim 22, wherein the Cu(II) complex is selected from the group consisting of bis(2-pyrrolealdehydeimino)copper(II), bis(2-pyrrolealdehydeimino)copper(II), bis(2-pyrrolealdehyde-iso-propylimino)copper(II), bis(2-pyrrolealdehyde-*t*-butylimino)copper(II), bis(2-pyrrolealdehydephenylimino)copper(II), bis(2-pyrrolylaldehyde-*n*-propylimino)copper(II), bis(2-pyrrolylaldehyde-*n*-butylimino)copper(II), bis(2-pyrrolylaldehydisobutylimino)copper(II), bis(2-pyrrolylaldehydm-trifluoromethylphenylimino)copper(II), bis(2-pyrrolylaldehydbenzylimino)copper(II), and bis(2-acetylpyrrolyl)copper(II).

24. The process of Claim 22, wherein the substrate is selected from the group consisting of glass, metals and ceramics, and silicon wafers coated with a barrier layer.

25. The process of Claim 22, wherein the reducing agent is selected from the group consisting of ammonia, ammonia/hydrogen mixtures, hydrazine, CO/hydrogen mixtures, 9-BBN, borane, dihydrobenzofuran, pyrazoline, diethylsilane, dimethylsilane, ethylsilane, phenylsilane, and silane.

26. The process of Claim 25, wherein the adsorbed copper complex is exposed to a reducing agent at a pressure of about 10 to about 760 millitorr, and the substrate is held at a temperature of about 100 °C to about 300 °C during the reduction.

27. A process for depositing copper on a substrate comprising heating a reducing agent and at least one Cu(II) complex of structure 1, structure 1 =



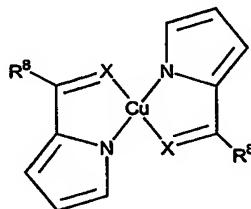
in the presence of a substrate, wherein:

30 X is O, and R8 is C1-C10 alkyl or substituted alkyl, or C6 to C12 aryl or substituted aryl; or
X is NR1 and R8 is H;

R¹ is selected from the group consisting of C₁-C₁₀ alkyl or substituted alkyl; C₆ to C₁₂ aryl or substituted aryl; allyl; benzyl; NHR³; and NR⁴R⁵; and

5 R³, R⁴, and R⁵ are independently selected from C₁-C₆ alkyl or substituted alkyl, and C₆ to C₁₂ aryl or substituted aryl.

28. An article comprising a substrate with a Cu(II) complex of structure 1 adsorbed on the surface or in or on porosity in the substrate, structure 1 =



10

wherein:

X is O, and R⁸ is C₁-C₁₀ alkyl or substituted alkyl, or C₆ to C₁₂ aryl or substituted aryl; or

X is NR¹ and R⁸ is H;

15

R¹ is selected from the group consisting of C₁-C₁₀ alkyl or substituted alkyl; C₆ to C₁₂ aryl or substituted aryl; allyl; benzyl; NHR³; and NR⁴R⁵; and

R³, R⁴, and R⁵ are independently selected from C₁-C₆ alkyl or substituted alkyl, and C₆ to C₁₂ aryl or substituted aryl.

20

29. An article of Claim 28, wherein the substrate is selected from the group consisting of glass, metals and ceramics, and silicon wafers coated with a barrier layer.

30. The process of Claim 24, wherein the barrier layer is selected from the group consisting of titanium nitride and tantalum/tantalum nitride.

25

31. The article of Claim 29, wherein the barrier layer is selected from the group consisting of titanium nitride and tantalum/tantalum nitride.

32. A process for preparing aryl pyrrolealdimines, comprising reacting an aqueous solution of 2-formylpyrrole with a water-immiscible primary amine, R'NH₂, wherein R' is C₆ to C₁₂ aryl or substituted aryl.

30